1969

Vaporization of Scandium Chloride

William Vincent Lucas

VAPORIZATION OF SCANDIUM CHLORIDE

BY

WILLIAM VINCENT LUCAS

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in
Chemistry, South Dakota State
University

1969

VAPORIZATION OF SCANDIUM CHLORIDE

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser Date

Head, Chemistry Department Date

ACKNOWLEDGMENTS

The author wishes to express his appreciation to:

Dr. L. H. Spinar under whose direction this work was carried out, and who helped in matters pertaining to the writing of this thesis.

Dr. A. L. Lingard of the South Dakota School of Mines and Technology for preparing the x-ray powder diffraction patterns.

Mr. Melvin Leitheiser and Mr. George Eastland for obtaining the infrared data.

Mrs. Dianna Randall for typing this thesis.

This work was carried on under a grant from the Institutional Funds for Research and Related Activities (IFRRA) made by the Research Committee of South Dakota State University. This support and that of the Department of Chemistry are gratefully acknowledged.

WVL

TABLE OF CONTENTS

	Page
INTRODUCTION	1
HISTORICAL BACKGROUND	3
EXPERIMENTAL APPARATUS AND PROCEDURES	7
Balance Design	7
Balance Calibration	13
Preparation of Scandium Chloride	17
Transfer of Scandium Chloride to Effusion Cells	18
RESULTS AND DISCUSSION	20
CONCLUSIONS	33
APPENDIX I	35
LITERATURE CITED	39

LIST OF TABLES

Table		Page
I.	Balance Calibration Values (mg/mv) . . .	15
II.	Vapor Pressure of Mercury	16
III.	Chloride Analyses and Infrared Data of Scandium Oxychloride and the Residues Formed During Vapor Pressure Trials . .	21
IV.	Comparison of d Values (Å) for Starting Material A, Residues B-2, B-3, B-4 and Material Prepared by Petru (15)	23
V.	Total Change in Weight During Vapor Pressure Trials	29
VI.	Vapor Pressure of Scandium Chloride . .	31

LIST OF FIGURES

Figures		Page
1.	Magnetically Controlled Microbalance .	8
2.	Balance Pan Assembly	11
3.	Sample Temperature as a Function of Reference Thermocouple Temperature . .	14
4.	Plot of Effusion Data for Trial B-1 . .	25
5.	Plot of Effusion Data for Trial B-1 . .	26
6.	Plot of Effusion Data for Trial B-3 . .	27
7.	Plot of Effusion Data for Trial B-4 . .	28
8.	Lid Device Used in Covering Orifice of Effusion Cell	36

INTRODUCTION

The purpose of this work was to determine the vapor pressure of scandium chloride. The scandium chloride was prepared by heating a mixture of $ScCl_3 \cdot 6H_2O$ and NH_4Cl under vacuum. The measurements on the resultant scandium chloride were made with a magnetically controlled microbalance. The system was evacuated to about 2×10^{-6} torr during the determinations.

Calibration, in terms of milligrams per millivolt, of the balance was obtained by weighing quartz effusion cells containing mercury before and after effusion and dividing the change in weight by the change in potential necessary to balance the cells before and after effusion. Calibration values also were obtained by using analytical weights. Vapor pressures of mercury and zinc were calculated as a check on the reliability of the data the balance yielded.

During the scandium chloride vapor pressure trials, the formation of scandium oxychloride was found to occur from the hydration and hydrolysis of scandium chloride. The scandium oxychloride remained in the quartz sample cells as a nonvolatile residue as a result of the effusion of scandium chloride from a mixture of scandium chloride and scandium oxychloride.

An attempt to measure the vapor pressure of a substance simultaneously with its molecular weight was inconclusive. A lid device that slid over the orifice of the effusion cell was used in this particular investigation.

HISTORICAL BACKGROUND

A method for determining vapor pressures was set forth by Knudsen in 1909 (1). The development (2), based on kinetic theory, involves the effusion of a gas through an ideal (small and infinitely thin) orifice into a vacuum. The assumption of an external vacuum permits one to neglect the re-entry of the effusate.

From kinetic theory, the number, ν, of molecules or atoms striking a unit surface area per unit time is given by:

$$\nu = \tfrac{1}{4}(P\bar{c}/kT) \qquad (1)$$

where, $\bar{c}$ is the average velocity, $(8RT/\pi M)^{\frac{1}{2}}$ cm/sec.

P is the pressure (atmospheres).

k is the Boltzmann constant, 1.38026×10^{-16} erg/deg.

T is the temperature (^{o}K).

R is the gas constant, 8.3144 joules/deg-mole.

M is the molecular weight of the gas.

The rate of mass transfer, m, is given by:

$$m = \nu M/N_o \qquad (2)$$

where, N_o is Avagadro's number, 6.02252×10^{23} molecules/mole.

Combining equations (1) and (2) yields:

$$m = P(M/2\pi RT)^{\frac{1}{2}} \qquad (3)$$

The ideal Knudsen effusion equation thus becomes:

$$P_K^* = m(2\pi RT/M)^{\frac{1}{2}} = \frac{1}{44.33a}(T/M)^{\frac{1}{2}}(w/t) \qquad (4)$$

where, P_K^* is the ideal Knudsen vapor pressure (atmospheres).

a is the orifice area (cm^2).

w/t is the rate of weight loss (g/sec).

Equation (4) is valid for conditions of "molecular flow", where the only interactions are those between molecules and walls. Molecular flow is achieved when the mean free path of the effusing molecules is of the order of ten times as large as the diameter of the hole.

As previously indicated, equation (4) is valid only for a cell with an ideal hole. When molecules effuse through a real hole, the hole exerts a channeling effect on the effusing vapor because the molecules with velocities nearly perpendicular to the axis of the hole are deflected by the hole walls. This channeling effect causes the number of molecules escaping from the cell to be less than that predicted by the ideal effusion equation. Clausing (3) provided a correction factor, W_o, to the ideal equation for the effect of real cylindrical orifices. Values of W_o have also been calculated for conical orifices (4,5). The inclusion of this factor into the effusion equation (4) yields:

$$P_K = \frac{1}{44.33aW_o} (T/M)^{\frac{1}{2}}(w/t) \qquad (5)$$

where P_K is the Knudsen vapor pressure (atmospheres).

Motzfeldt (6) incorporated additional correction factors into the effusion equation to yield the equilibrium

vapor pressure, P_{eq}. The additional factors yield:

$$P_{eq} = \left[1 + f\left(\frac{1}{\alpha} + \frac{1}{W_A} - 2\right)\right] P_K \qquad (6)$$

where $f = W_o a/A$.

A is the sample area (cm^2).

α is the accomodation coefficient.

W_A is the Clausing factor for the cell.

The value of the accomodation coefficient is needed to obtain equilibrium vapor pressures from equation (6). An acceptable alternative is the measurement of P_K for several hole sizes followed by extrapolation of P_K to zero hole size (7). At this point, factor f is negligible and equation (6) reduces to equation (5).

The vapor pressure of scandium chloride has been investigated by Fischer and co-workers (8). The measurements were carried out using a molybdenum bell containing the scandium chloride immersed in melted tin. The molybdenum bell was suspended from a pulley by a steel wire. As the temperature of the system increased, the pressure inside the bell increased, thus raising the level of the bell. The bell was returned to its original level by allowing argon into the previously evacuated system. This amount of argon, as measured by a manometer, corresponded to the vapor pressure of the scandium chloride inside the bell.

The vapor pressure equation for scandium chloride in the range 1065 to 1239°K (792 to 966°C) was determined to be:

$$\log p \text{ (torr)} = \frac{-65,000}{4.57T} + 14.37 \qquad (7)$$

The corresponding pressure range is 12 to 714 torr. These pressures are considerably above the "molecular flow" region. No reports of vapor pressure data on scandium chloride in the Knudsen region of pressures have been found.

EXPERIMENTAL APPARATUS AND PROCEDURES

Weight losses in this work were measured using a magnetically controlled microbalance based on a design described by Spinar (9). The microbalance is contained in a borosilicate glass envelope which served as a vacuum chamber.

The vacuum was achieved using a Kinney Model KC-2 forepump and a NRC[1] Model H-2-SP oil diffusion pump. A NRC Model 721 thermocouple vacuum gauge was used to monitor the forepump pressures. At a pressure of 10^{-2} torr the oil diffusion pump, using Narcoil-40 oil, was started. The system pressure then was measured with a NRC Model 524-1 cold cathode gauge and read on a NRC Model 724 gauge control. Operating pressures were of the order of 10^{-6} torr. A liquid nitrogen trap was used to achieve the lower limits and to keep contaminants out of the oil.

Balance Design

The magnetically controlled microbalance used in this work is sketched in Figure 1. A cradle made of six millimeter Pyrex brand tubing is held in place by three

---

[1]The name of the NRC Equipment Corporation was changed to Norton Vacuum Equipment Division on January 1, 1968.

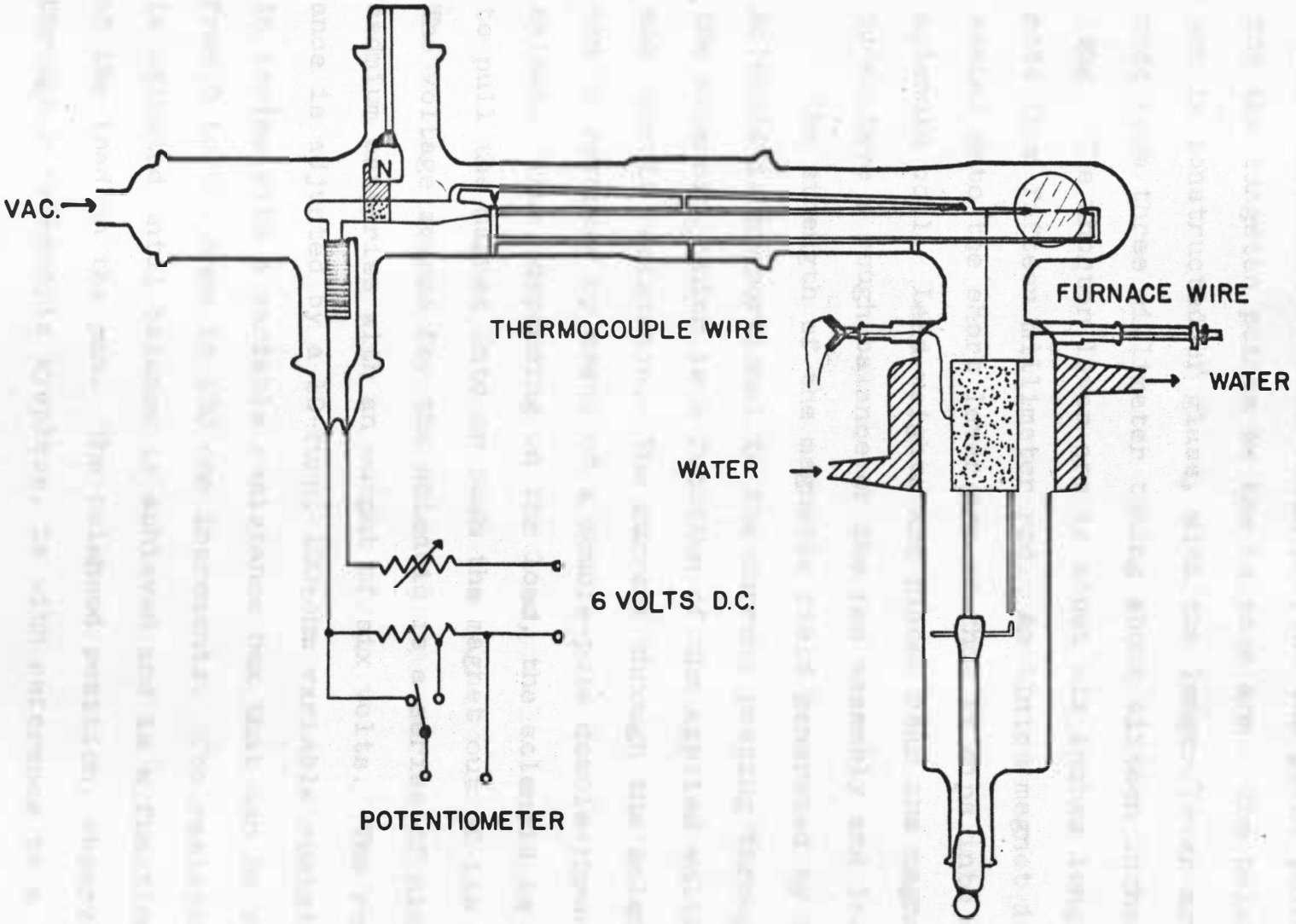

FIGURE I. MAGNETICALLY CONTROLLED MICROBALANCE

pegs in the vacuum envelope and Apiezon type W wax. The cradle supports two cups which provide the pivot points for the tungsten points on the balance arm. The balance arm is constructed of glass, with the longer lever arm made from three millimeter tubing about sixteen inches long. The shorter lever arm is about six inches long and made from fifteen millimeter rod. An Alnico magnet is sealed onto the short lever arm so that it dips into a solenoid coil. Lead weights are placed near the magnet to achieve a rough balance of the pan assembly and load.

The strength of the magnetic field generated by the solenoid is proportional to the current passing through the solenoid, which is a function of the applied voltage and circuit resistance. The current through the solenoid can be reversed by means of a double-pole double-throw switch. Thus, depending on the load, the solenoid is used to pull the magnet into or push the magnet out of its core. The voltage source for the solenoid is a series of nickel-cadmium batteries with an output of six volts. The resistance is adjusted by a 10-turn, 100-ohm variable resistance in series with a variable resistance box that can be varied from 0 to 600 ohms in 100 ohm increments. The resistance is adjusted until balance is achieved and is a function of the load on the pan. The balanced position, observed through a telescopic eyepiece, is with reference to a

fixed pointer on the cradle. The current necessary for the balance of a pan load is read as a potential drop across a 0.1 ohm manganin wire resistor with high current carrying capacity. A Honeywell Model 2746 portable potentiometer was used to measure the potential drop to the nearest 0.01 millivolt.

The quartz balance pan and quartz sample cell (Figure 2) are suspended from the balance arm into a furnace by a B&S 28 gauge nichrome wire. The balance pan is approximately 1 3/8 inches in diameter and 2 inches high. The sample cells are constructed from 13 millimeter inner diameter quartz tubing and 2 millimeter thick quartz plate. The cells are about 20 millimeters high. A glass drill bit was used to put a small orifice in each of the cells. The dimensions of the holes were measured with an eyepiece graduated in 0.1 millimeter divisions. The semi-apex angle of the right cone of which the conical orifice is a truncated section was determined to be approximately 15 degrees. The Clausing correction factor, W_o, was then found from a plot of W_o versus $\log(L/r_o)$ as given by Freeman (5). L is the length of the hole and r_o is the diameter of the smaller end of the conical orifice.

Access to the pan assembly is made through a ₸103/60 ground glass joint sealed with Apiezon type W wax. A water

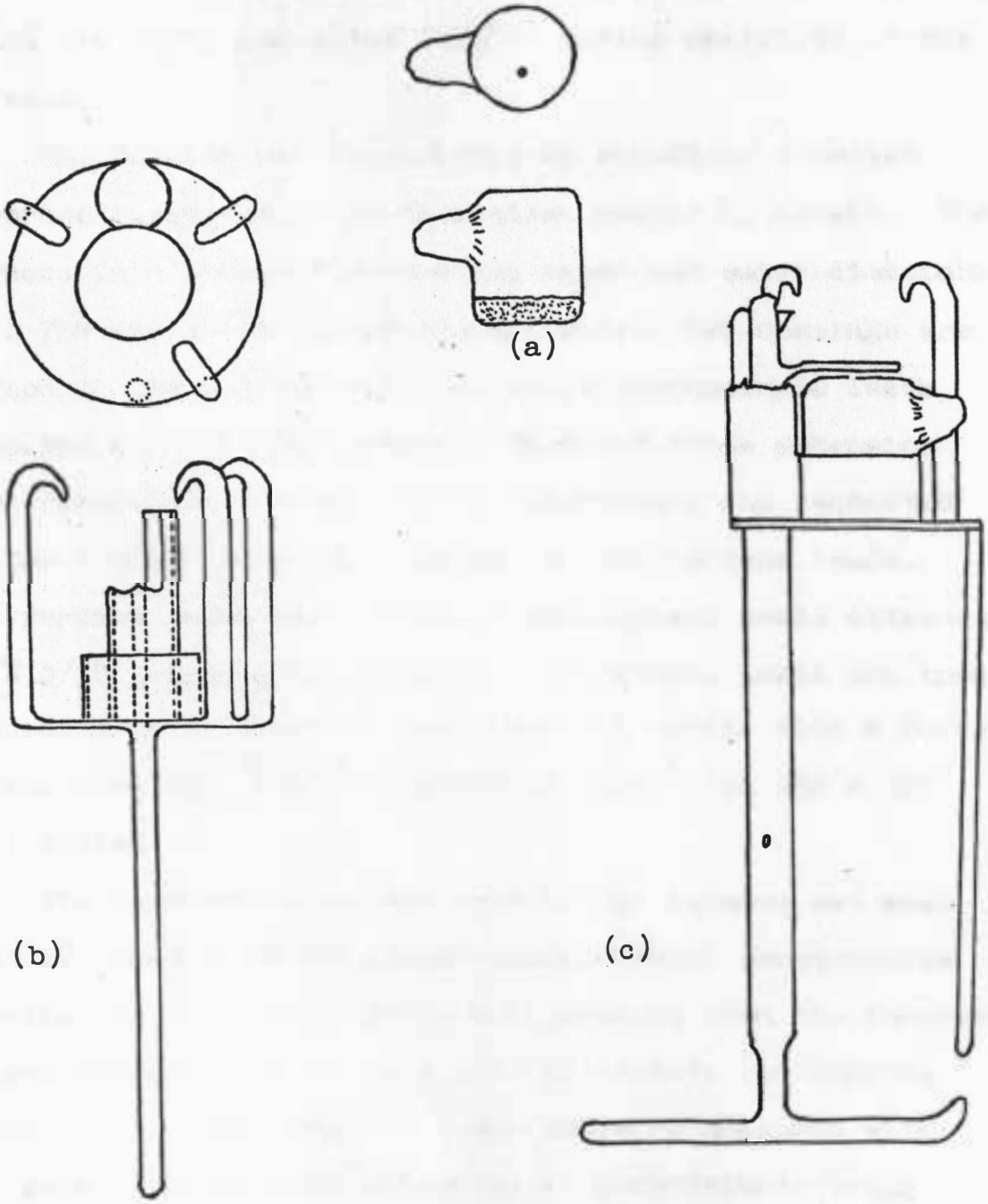

Figure 2. Balance Pan Assembly

(a) Quartz sample cell
(b) Balance pan (quartz)
(c) Sample cell in pan

jacket about the joint keeps the temperature of the wax below its softening point (100°C) during operation of the furnace.

The furnace was constructed by embedding a coiled Nichrome furnace wire in Sauereisen Number 63 cement. The furnace is 5 inches high and has inner and outer diameters of 1 7/8 and 2 1/4 inches respectively. Two openings are formed in the furnace walls to admit thermocouple leads into the core of the furnace. Threaded brass extension rods running up the outside of the furnace and connected to the furnace wire are attached to the furnace leads. The furnace leads are welded in Kovar-glass seals attached to ₸10/30 ground glass joints. The furnace leads are then connected to a variable transformer in series with a Barber-Colman Amplitrol brand temperature controller and a 120 volt outlet.

The temperature in the core of the furnace was measured by using a B&S 28 gauge chromel-alumel thermocouple terminating on binding posts well removed from the furnace. Copper extension wires were used to connect the binding posts to the potentiometer. The voltages measured with the potentiometer were converted to temperatures using standard calibration tables for chromel-alumel thermocouples (10). The thermocouple was positioned about one centimeter above the sample cell when the pan load was

balanced. To obtain the temperature of the sample, another thermocouple was placed on the pan, without a cell present. The temperature of the measuring thermocouple was plotted as a function of the temperature on the pan. The temperature measured by the reference thermocouple can thus be converted to the sample temperature by the use of Figure 3.

The output of the reference thermocouple was also used to operate the Amplitrol temperature controller. The temperature controller operated a relay which opened and closed the heater circuit. Stepless potentiometric control of the furnace temperature to about two degrees Celsius was achieved with this arrangement.

Balance Calibration

Since the balance system just described does not yield absolute weights, it was necessary to obtain a relationship between the weight loss of a sample cell and the change in the number of millivolts needed to obtain a balance of the cell before and after weight loss.

The calibration of the balance was carried out with mercury as the vaporizing substance. Sample cells, as shown in Figure 2 (a), were filled with mercury via a side arm, sealed with an oxygen-hydrogen flame, and weighed to the nearest 0.1 milligram. The cells were placed on the balance pan, the access joint sealed, and the system

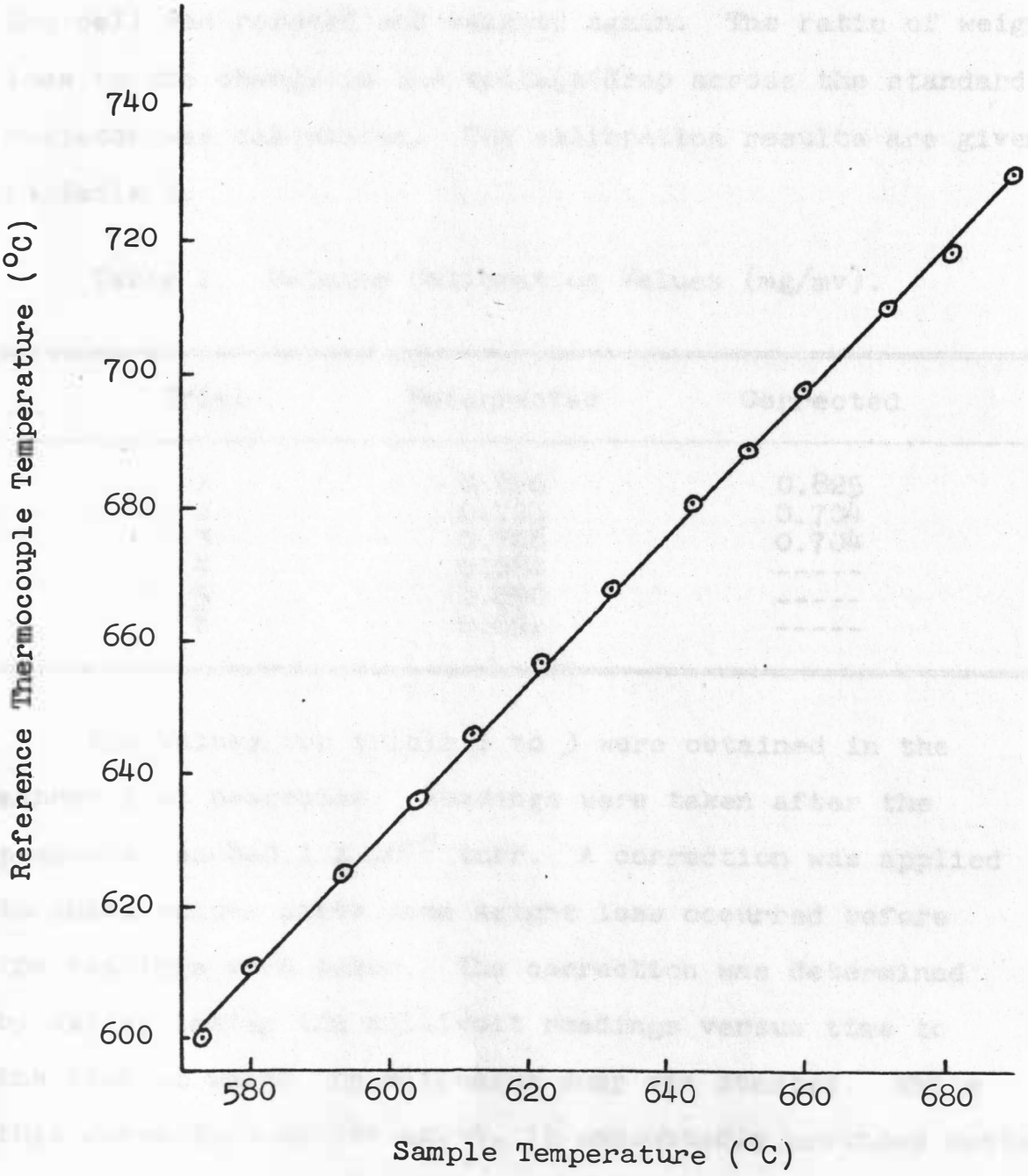

Figure 3. Sample Temperature as a Function of Reference Thermocouple Temperature.

evacuated. The mercury weight loss was followed by the variable resistance and the potentiometer. After a trial, the cell was removed and weighed again. The ratio of weight loss to the change in the voltage drop across the standard resistor was calculated. The calibration results are given in Table I.

Table I. Balance Calibration Values (mg/mv).

Trial	Uncorrected	Corrected
1	0.890	0.825
2	0.723	0.704
3	0.706	0.704
4	0.684	-----
5	0.690	-----
6	0.691	-----

The values for trials 1 to 3 were obtained in the manner just described. Readings were taken after the pressure reached 1×10^{-5} torr. A correction was applied to these values since some weight loss occurred before the readings were taken. The correction was determined by extrapolating the millivolt readings versus time to the time at which the diffusion pump was started. While this correction is not exact, it undoubtedly provides better sensitivity values than the uncorrected values. The first trial was completed with a rather small weight loss, which

may explain why it does not agree well with the other values. If the corrections applied to these three sensitivity values were too small, then just such a result would be expected for a trial in which only a small amount of weight loss occurred. The correction factor may have been too small because a small amount of mercury was lost after the last millivolt value was recorded. This additional weight loss occurred while the diffusion pump was cooling under vacuum and when the access joint was heated so that it could be removed.

The last two calibration trials with mercury (2 and 3) were also used as a check on the accuracy with which the vapor pressure of a substance could be measured. Equation (5) on page 4 was used to obtain the vapor pressure values. The parameters used in equation (5) and the resulting values of P_K are given in Table II.

Table II. Vapor Pressure of Mercury.

$a(x10^3\ cm^2)$	W_o	T(°K)	M	w/t(mg/hr)	$P_K(x10^3$ torr)
0.964	0.71	298	200	0.245	2.1
6.22	0.73	298	200	1.40	1.9

Vapor pressures for mercury of 1.691×10^{-3} torr at 24°C and 2.000×10^{-3} torr at 26°C are reported (11). The

measured vapor pressures indicate that it is possible to obtain good results with the present microbalance system.

Weight loss data for zinc treated in the same manner gave a vapor pressure value of 0.250 torr at 439°C. The value calculated from data given by Kelley (12) is 0.273 torr. This result also indicates that good vapor pressure data are obtainable with the present system at elevated temperatures. In this case, the error can be attributed to the fact that 0.250 torr is somewhat above the Knudsen region of pressures.

Preparation of Scandium Chloride

The scandium chloride used in this work was prepared by a method which Taylor and Carter (13) used to prepare lanthanon halides. No literature references were found in which scandium chloride was prepared in this manner. Scandium oxide and ammonium chloride were dissolved in 6N hydrochloric acid in the ratio of 12 moles of ammonium chloride to 1 mole of scandium oxide. The resulting solution was evaporated to near dryness on a hot plate, redissolved in concentrated hydrochloric acid, and evaporated to dryness. This mixture was ground in a mortar and sealed in a glass sublimation tube. The ammonium chloride was sublimed from the scandium chloride at temperatures starting at 150°C and finishing at 400°C. The scandium chloride was then

heated at 450°C for one-half hour to ensure that the ammonium chloride sublimation was complete. During the sublimation process, the system pressure was kept below 1×10^{-1} torr. The portion of the sublimation tube containing the slightly gray scandium chloride was sealed at a pressure of 2×10^{-2} torr.

Chloride analyses carried out by the Mohr method gave values of 1.858×10^{-3} and 1.448×10^{-3} equivalents of chloride. From the sample weights used, the calculated values were 1.843×10^{-3} and 1.473×10^{-3} equivalents of chloride respectively. From these results, the prepared scandium chloride was considered to be essentially $ScCl_3$.

Transfer of Scandium Chloride to Effusion Cells

It was necessary to keep the scandium chloride dry at all times. Hydrated scandium chloride does not lose all of its water by heating under vacuum, but rather decomposes to scandium oxychloride and scandium oxide (14). For this reason, the following procedures were taken to limit the hydration of the scandium chloride.

The scandium chloride was transferred to the effusion cells in a glove bag under nitrogen. The nitrogen was passed through a calcium chloride-phosphorus pentoxide drying tube to remove water. The cells were filled via a side arm, after which a flow of nitrogen was maintained

over the scandium chloride until the cells were ready to be sealed with an oxygen-hydrogen flame. After the cells were sealed, melted naphthalene was used to seal the orifices. The naphthalene covering prevented moisture from reaching the scandium chloride. After the cells were in the balance assembly, the naphthalene was removed under vacuum.

RESULTS AND DISCUSSION

Five trials were completed in an attempt to obtain vapor pressure data on scandium chloride. The trials are designated as: A-1, B-1, B-2, B-3, and B-4. Starting material A was obtained by subliming scandium chloride as prepared by the method described on page 17. The sublimation was carried out at 850°C in a quartz tube under vacuum for about one hour. A pure white crystalline material resulted. Very little weight loss was found using material A (Trial A-1). Starting material B was prepared as described on page 17, but was not sublimed. Trials B-1, B-2, B-3, and B-4 were carried out with this preparation of scandium chloride. A nonvolatile residue was left in the effusion cells after each trial.

Material A was found to contain 36.1% chloride. When converted to scandium oxide by ignition in air at 800°C, sample A gave a gravimetric factor for $Sc_2O_3/2ScOCl$ = 0.707. Pure scandium oxychloride is 36.8% chloride and gives a gravimetric factor of 0.715 for $Sc_2O_3/2ScOCl$. Thus material A was found to be scandium oxychloride.

Infrared spectra were obtained for Nujol mulls of the residues on the Perkin Elmer Model 521 Infrared Spectrophotometer. The chloride analyses and infrared data of

scandium oxychloride (material A) are compared in Table III with the nonvolatile materials resulting from the effusion trials. The silver chromate endpoint of the Mohr method was difficult to detect and may have caused the residue from B-3 to appear too high in chloride content. A small amount of the residues resulting from the trials carried out on starting material B was insoluble, thus causing the gravimetric determination of the chloride content of the residues from trials B-2 and B-4 to be slightly low in comparison to scandium oxychloride.

Table III. Chloride Analyses and Infrared Data of Scandium Oxychloride and the Residues Formed During Vapor Pressure Trials.

Sample	% Chloride	Absorption Maxima (cm^{-1})
A	36.1	605 M, 475 S
B-2	29.6	605 M, 475 S
B-3	41.8*	545 M
B-4	34.0	605 M, 475 S

* The chloride analysis on this residue was carried out by the Mohr method. Others were determined gravimetrically by precipitation of silver chloride.

M = moderate; S = strong

X-ray diffraction data for the residues indicate that they are primarily scandium oxychloride. The x-ray powder diffraction patterns were prepared by Dr. A. L. Lingard

of the Engineering and Mining Experiment Station at the South Dakota School of Mines and Technology using a camera of diameter 114.6 millimeter and a copper source with a nickel filter. The d values were measured in this laboratory. The x-ray powder pattern of material A is compared in Table IV with those of the residues and with the values obtained by Petru and co-workers (15). Petru thermally decomposed the hexahydrate of scandium chloride under a nearly dry nitrogen atmosphere. He claimed that ScOCl was formed at about 200°C and was immediately converted to $Sc(OH)_xCl_y$ by traces of moisture in the gas stream. This transformation did not significantly affect the x-ray diffraction pattern between 200°C and 400°C. The x-ray data given by Petru are for a mixture of ScOCl and $Sc(OH)_xCl_y$ at 310°C. A comparison of the d values reported for scandium chloride (16) and scandium oxide (17) with those tabulated on the following page indicates that they are present in only minor amounts, if at all.

From the data presented, it is concluded that the residue in the effusion cells is scandium oxychloride. While the infrared data for the residue from B-3 are not in good agreement with those of scandium oxychloride (material A), the x-ray diffraction data show the two materials to be very similar.

Table IV. Comparison of d Values (Å) for Starting Material A, Residues B-2, B-3, B-4 and Material Prepared by Petru (15).

A	B-2	B-3	B-4	Petru
8.20 vs	8.17 s	8.18 s	8.18 vs	7.89 (4)
6.47 vw	6.46 w-m	6.46 w	----	----
----	5.54 vw	----	----	----
----	4.48 vw	4.50 vw	----	----
3.96 vw	----	----	3.94 vw	----
----	3.76 w-m	3.78 w	----	----
3.58 vs	3.60 s	3.60 s	3.56 vs	3.53 (4)
----	3.34 w	3.35 vw	----	3.36 (1)
2.93 vvw	----	----	----	----
2.84 vvw	2.78 w	2.80 vvw	2.84 vw	2.79 (2)
2.72 vw	----	----	----	----
2.66 vs	2.63 m	2.64 m-s	2.64 s	2.59 (2)
----	2.52 vvw	----	----	----
2.49 m	2.46 w	2.48 w-m	2.48 w-m	2.43 (1)
2.25 w	----	----	2.24 w	2.29 (2)
2.15 w-m	2.12 w	2.13 w	----	2.19 (1)
2.05 w	2.06 vw	----	----	2.07 (1)
1.99 m	1.98 w-m	1.98 m	1.98 m	1.98 (3)
1.94 w	----	1.92 vvw	1.92 w	1.92 (2)
1.89 s	1.87 w	1.88 w-m	1.88 w-m	1.86 (1)
----	1.78 vvw	----	----	1.79 (1)
1.74 w-m	1.72 w	1.73 w-m	1.73 w-m	----
1.64 vvw	1.68 vvw	----	1.69 vw	1.65 (2)
1.61 vvw	----	----	----	1.62 (2)
1.59 m	1.58 w	1.58 w-m	1.58 m	1.58 (2)
1.56 w-m	1.55 w	1.55 w	1.56 w	----
1.51 w	----	----	----	----
1.46 vw	----	----	1.45 vw	1.45 (1)
1.43 vw	----	----	----	1.45 (1)
----	----	----	----	1.39 (1)
1.32 vw	----	----	----	----
1.31 w-m	1.30 w	1.30 w	1.30 w-m	1.28 (1)
1.29 vw	----	----	----	----

s = strong, m = moderate, w = weak, v = very; Petru rated intensities on a scale of (1) to (5), with (5) being the most intense.

The hydration and hydrolysis of scandium chloride offer the best explanation for the appearance of scandium oxychloride in the effusion cells. It is likely, that in working in a glove bag, under a "dry" nitrogen atmosphere, the scandium chloride picks up moisture each time a cell is loaded. A hydrolysis product, such as $Sc(OH)Cl_2$, or a hydrated form of $ScCl_3$ then decomposes at a temperature of less than 500°C yielding scandium oxychloride (14, 15, and 18).

The thermal decomposition to scandium oxychloride thus should have been completed before the weight loss data for the effusion trials were taken. Since the furnace is of a porous nature and absorbs a good deal of air when cooled, it was heated to about 550°C to drive off the air before starting the diffusion pump. Therefore, the cell was kept at 550°C for several hours under a vacuum of from 1×10^{-3} to 5×10^{-6} torr before any data were taken.

The usable weight loss data from trials B-1, B-3, and B-4 are plotted in Figures 4, 5, 6, and 7. The temperature appearing in these figures has been corrected by use of Figure 3. The data shown in these figures result from the effusion of scandium chloride from a mixture of scandium chloride and scandium oxychloride.

As can be seen in Table V, the total weight loss was less in successive determinations. This is consistent with

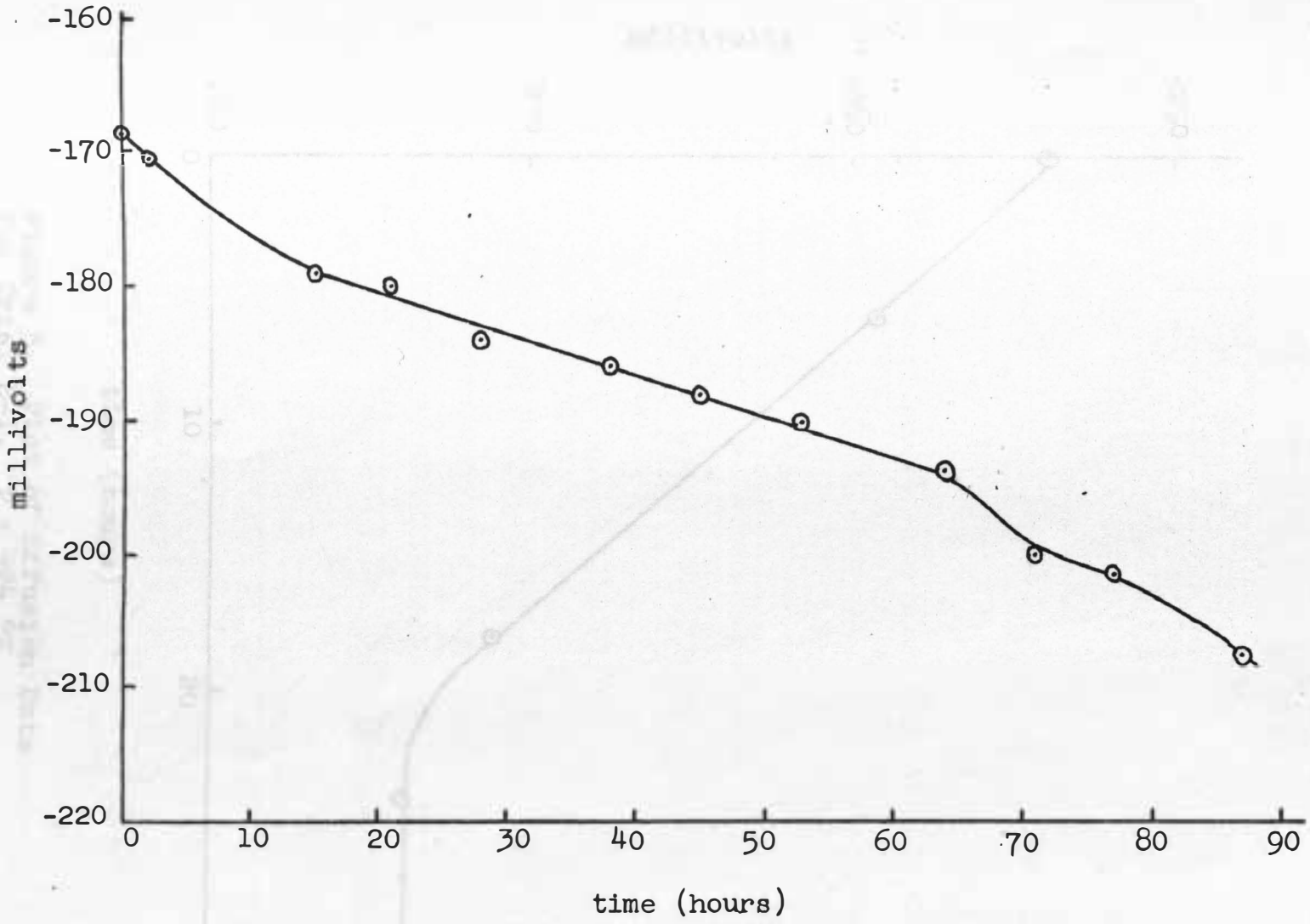

Figure 4. Plot of Effusion Data for Trial B-1. T = 885 ^{o}K.

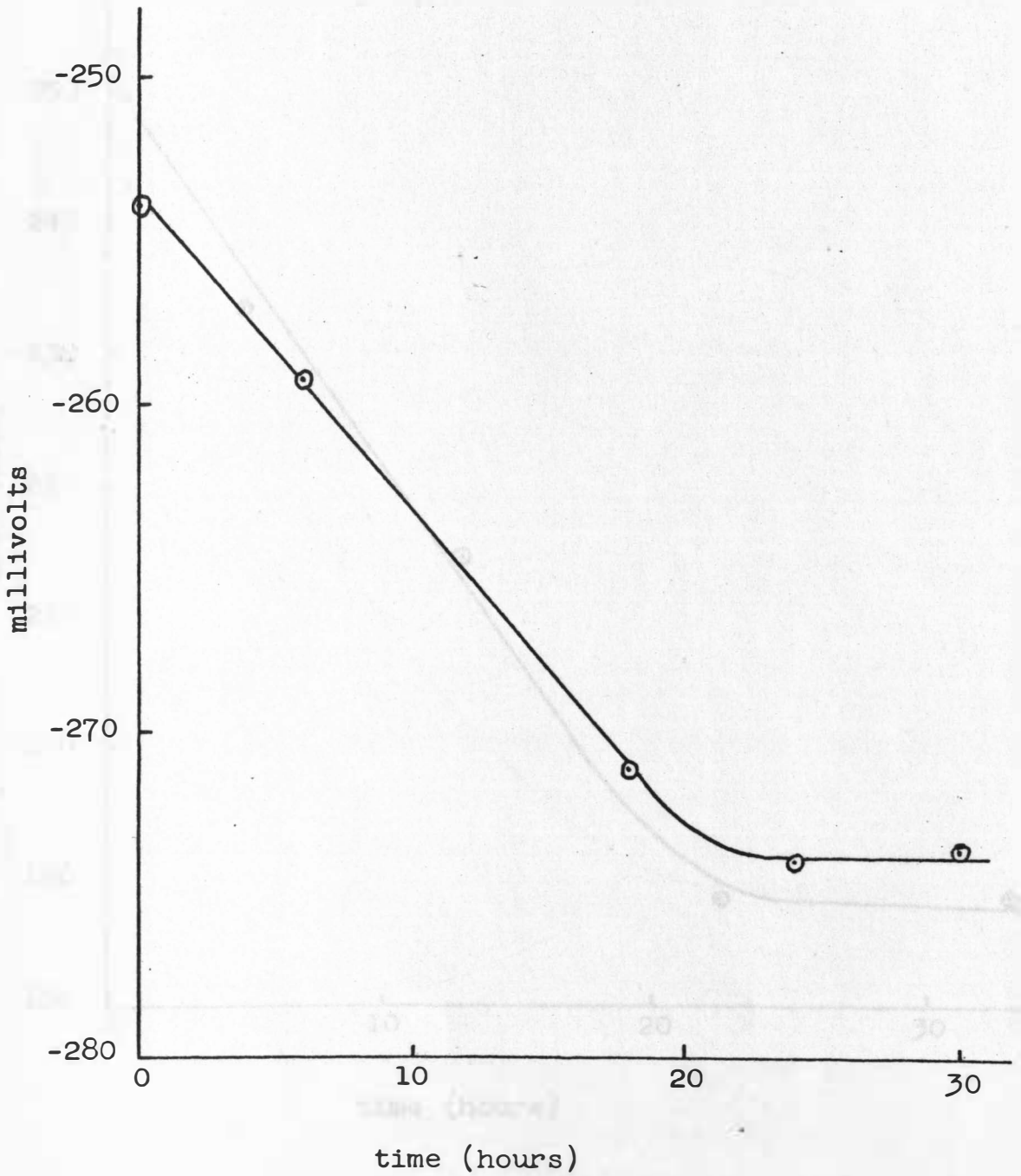

Figure 5. Plot of Effusion Data for Trial B-1. T = 924 ^{o}K.

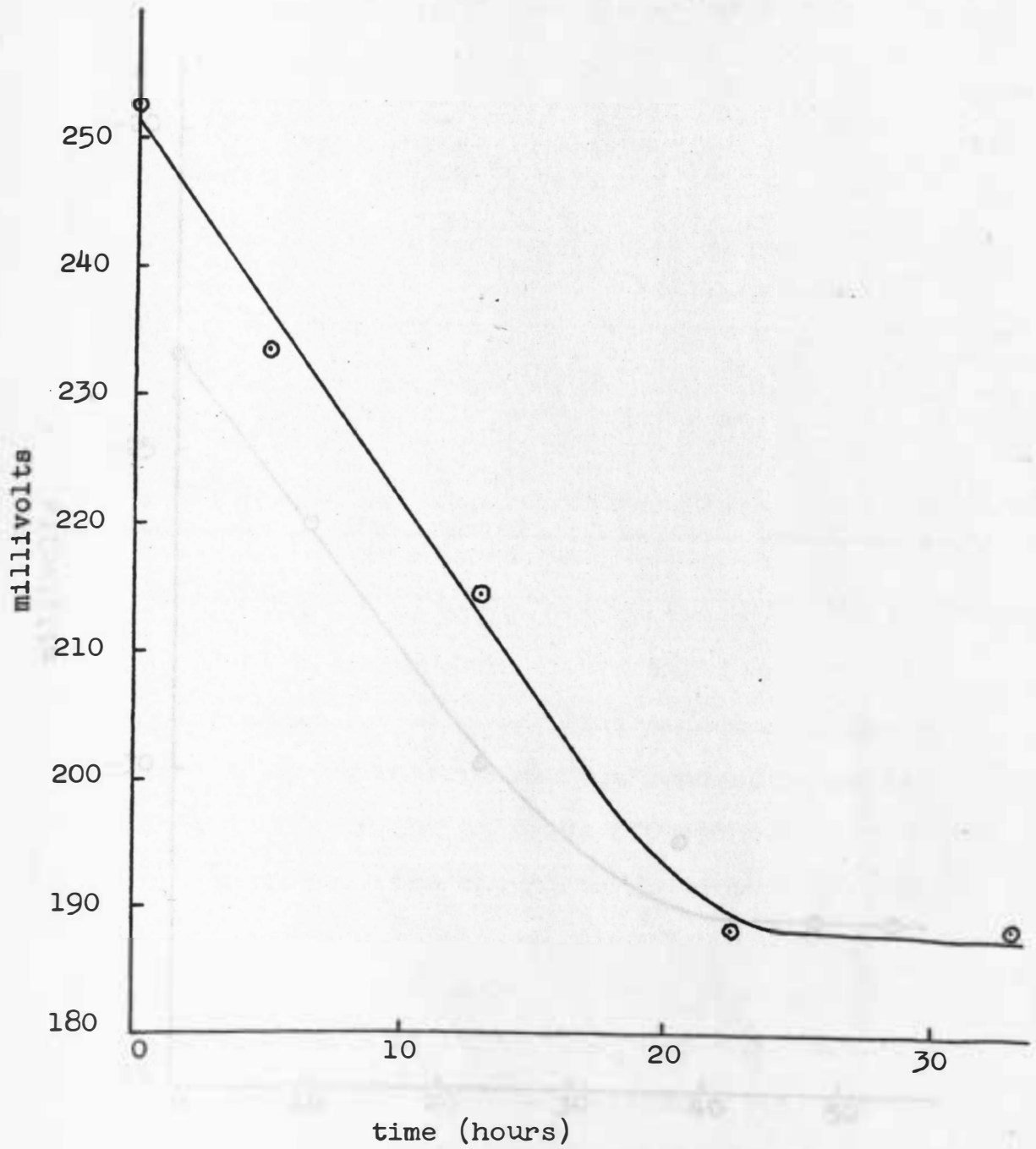

Figure 6. Plot of Effusion Data for Trial B-3. T = 924 ^{o}K.

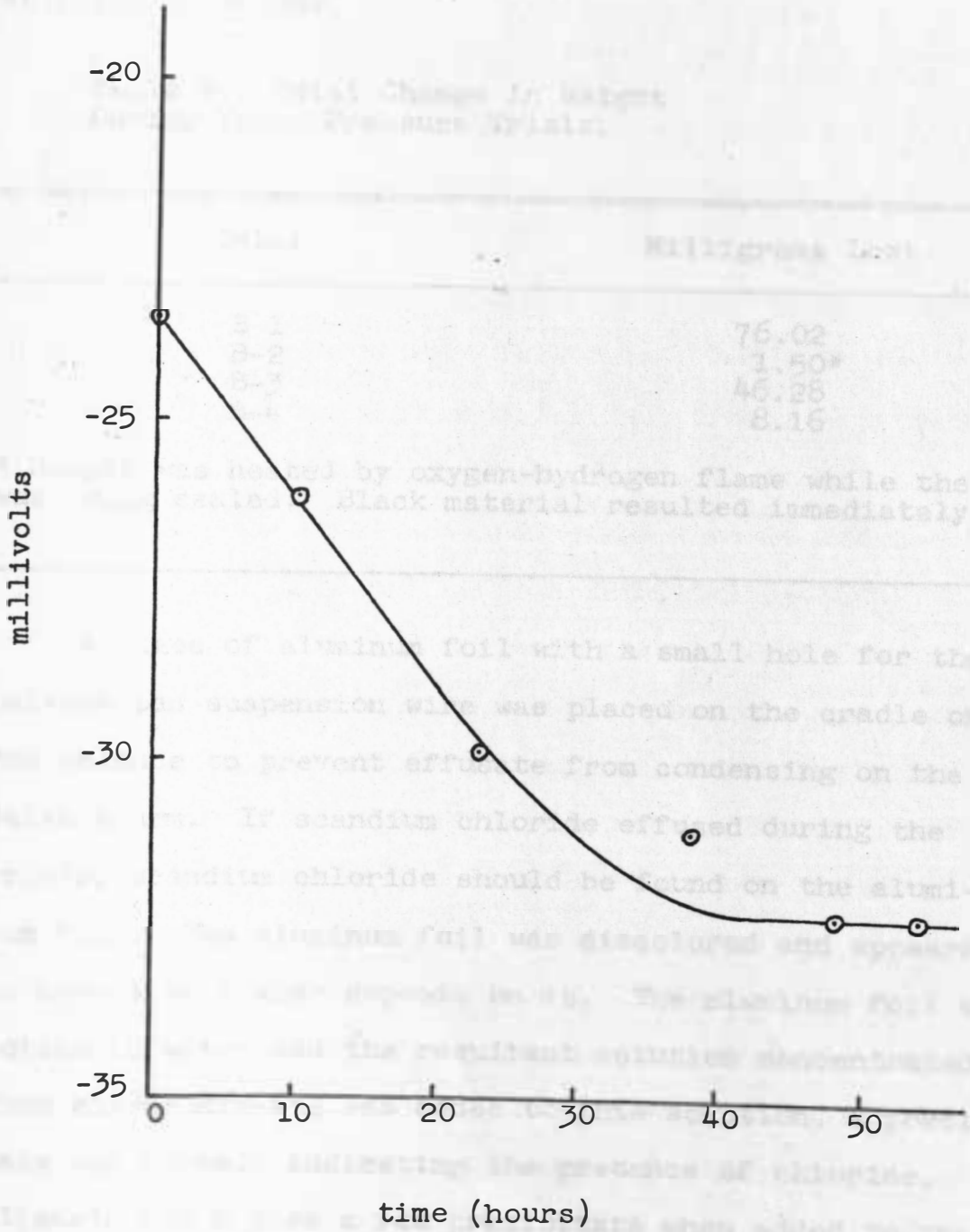

Figure 7. Plot of Effusion Data for Trial B-4. T = 918°K.

the situation where more scandium chloride is being hydrolyzed in each successive trial, leaving less scandium chloride to effuse.

Table V. Total Change in Weight During Vapor Pressure Trials.

Trial	Milligrams Lost
B-1	76.02
B-2	1.50*
B-3	46.28
B-4	8.16

* Sample was heated by oxygen-hydrogen flame while the cell was being sealed. Black material resulted immediately.

A piece of aluminum foil with a small hole for the balance pan suspension wire was placed on the cradle of the balance to prevent effusate from condensing on the balance arm. If scandium chloride effused during the trials, scandium chloride should be found on the aluminum foil. The aluminum foil was discolored and appeared to have a yellowish deposit on it. The aluminum foil was boiled in water and the resultant solution concentrated. When silver nitrate was added to this solution, a precipitate was formed, indicating the presence of chloride. Alizarin Red S gave a red precipitate when added to the

solution, indicating the presence of either aluminum or scandium. A color change from purple to yellow-orange was observed when a small amount of an aqueous murexide solution was added to the solution obtained from the aluminum foil. This test (19) confirmed the presence of scandium and thus the effusion of scandium chloride from the cell.

Since the effusion of scandium chloride from the cell has been shown, the weight loss data provide values for the vapor pressure of scandium chloride. The rate of weight loss in Figures 4 through 7 appears to be constant. Deviations from a constant rate of weight loss is assumed to be due to balance instability. In trial B-1 at 885°K, the rate of weight loss was taken as the slope of the curve during the middle of the trial when the rate was rather constant. The rate of weight change during the other trials was calculated in a similar manner. The values obtained for the vapor pressure of scandium chloride are given in Table VI.

The straight line portions of Figures 4 through 7 indicate that the scandium chloride effusion rate is not dependent on the concentration of scandium oxychloride. The apparent reduction in effusion rate just before effusion stops is probably because effusion had stopped some time prior to balancing the cell.

Table VI. Vapor Pressure of Scandium Chloride.

Trial	a($\times 10^3$ cm^2)	W_o	T(^oK)	M	w/t(mg/mv)	P_K($\times 10^3$ torr)
B-1	3.32	0.72	885	151.3	0.21	1.0
B-1	3.32	0.72	924	151.3	0.66	3.2
B-3	3.32	0.72	924	151.3	2.0	9.9
B-4	5.67	0.73	918	151.3	0.18	0.50

As mentioned in Table V, the sample used for trial B-2 was heated with the oxygen-hydrogen torch during the sealing of the cell. The weight loss of this trial was not sufficient to calculate a vapor pressure for scandium chloride. The rather poor vapor pressure value yielded by trial B-4 was probably, in part, due to a power failure at the university. The trial had just been started when the power failed and went unnoticed for about one-half hour. The result was that the balance system was no longer under a vacuum and that the vacuum system was out of order for about one week. It is likely that the sample hydrated to a further extent than originally, since the naphthalene covering had been removed by this time. When trial B-4 was finally started, there appeared to be a small amount of effusion at 550°C, even after several hours at that temperature. This was not the case with the other trials.

On the basis of these arguments, the vapor pressure of scandium chloride is 1 x 10^{-3} torr at 885°K and 6.6 x 10^{-3} torr at 924°K. The heat of sublimation for scandium chloride is calculated to be 78 kcal/mole between 885°K and 924°K using the relationship:

$$\log p = -\Delta H_{sub}/2.303RT + C \qquad (8)$$

CONCLUSIONS

The results of this project include a simple preparation of scandium chloride, the x-ray powder diffraction pattern of scandium oxychloride, and an estimate of the vapor pressure of scandium chloride.

Difficulty was encountered in the measurement of vapor pressures of scandium chloride because of its very hygroscopic nature. This property led to the formation of scandium oxychloride during the effusion trials, and the subsequent characterization of scandium oxychloride by x-ray powder diffraction.

Future work on the determination of scandium chloride vapor pressures should include provisions for keeping the scandium chloride completely anhydrous. This condition could probably be approximated if the scandium chloride was transferred to a number of small vials in a good dry box. This step should prevent additional hydration of the sample with each successive vapor pressure trial. It would also be advisable to try effusion cells made of a material other than quartz, such as graphite or stainless steel (20). Fischer (8) noted that scandium chloride attacked quartz at high temperatures, although this phenomenon was not observed in this laboratory. An additional advantage of

such cells may be the ability to seal them in a manner which reduces the possibility of scandium chloride hydration.

APPENDIX I

SIMULTANEOUS DETERMINATION OF MOLECULAR WEIGHT AND VAPOR PRESSURE

A lid device shown in Figures 2(c) and 8 was used in several attempts to obtain the vapor pressure and molecular weight of mercury and zinc simultaneously. In principle, the apparent weight of the effusion cell should be greater when it is open than when it is closed due to the downward force exerted by the escaping molecules. The expressions of interest are (2):

$$P = 2(\Delta W)(g)/r^2 \qquad (9)$$

and

$$M = RT(w/t)^2/2(\Delta W)^2 g^2 \qquad (10)$$

where, P is the pressure (dynes/cm^2).

ΔW is the difference in the apparent weight of the open and closed cell (grams).

g is the gravitational constant, 980.665 cm/sec^2.

r is the radius of the small end of the orifice (cm).

The cells were loaded with mercury and zinc through a side arm and sealed with an oxygen-hydrogen torch. The cell was then placed on the balance pan, the access joint sealed, and the balance system evacuated to 1 x 10^{-3} torr with the mechanical pump. The furnace was heated to the

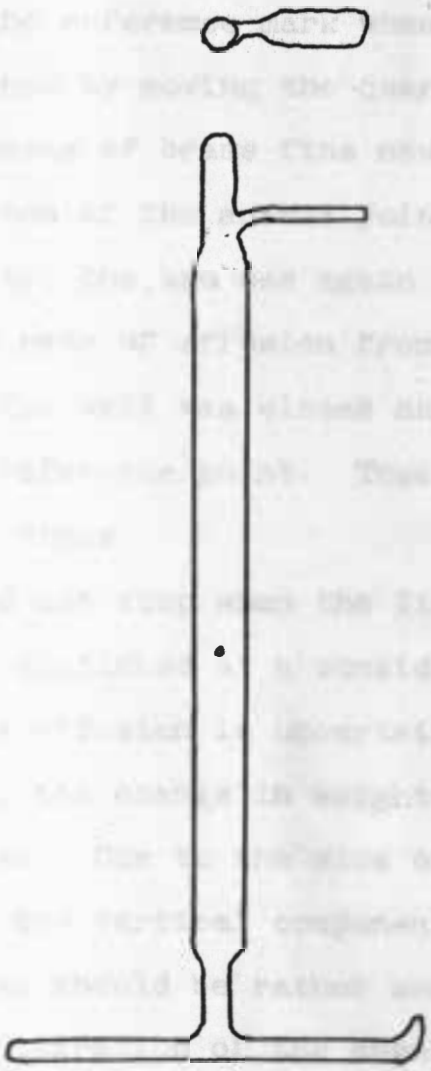

Figure 8. Lid Device Used in Covering Orifice of Effusion Cell.

desired temperature and then the oil diffusion pump was turned on to achieve a vacuum of less than 1×10^{-5} torr. The current through the solenoid was adjusted to bring the balance arm to the reference mark when the cell was closed. The cell was opened by moving the quartz lid across the top of the cell by means of brass fins mounted on a ground glass joint on the bottom of the access joint. After the balance regained stability, the arm was again brought to the reference point. The rate of effusion from the open cell was also measured. The cell was closed and the balance arm adjusted to the reference point. These procedures were repeated several times.

Effusion did not stop when the lid covered the orifice of the cell, but continued at a considerable rate. The direction of this effusion is uncertain. If an upward component exists, the change in weight of the cell would be less than expected. Due to the size of the lid in comparison to the hole, the vertical component of the path of escaping molecules should be rather small. It is necessary to consider an integration of the angular distribution of the effusate from an open cell even if the upward component of the effusate from the "closed" cell is negligible.

A limitation inherent in this method lies in the accuracy with which W can be measured even under nearly ideal conditions. W is usually a small number resulting from

the difference in two large values. A small absolute error in ΔW gives rise to a large percentage error in the calculated pressure or molecular weight. An indication of this problem can be seen from some results. The vapor pressure of mercury at 150°C was found to be 0.50 torr by this method. The accepted vapor pressure is 2.8 torr. This result would indicate that ΔW was too small by a factor of almost six (see equation 9). The molecular weight of zinc was found to be 15.1 and 31.0 g/mole at 439°C. The accepted molecular weight of zinc is 65.38 g/mole. This result shows that ΔW was too large by a factor of from two to four (see equation 10). The w/t data were found to be valid because of the rather good agreement obtained for the vapor pressure of zinc (0.250 torr at 439°C) as mentioned in the experimental section of this thesis.

In the trials just mentioned using mercury and zinc as the effusing substances, the vapor pressures were quite high, and it is questionable whether these pressures are within the Knudsen range of pressures. If the vapor pressures are increased by raising the temperatures to get larger values for ΔW, the pressures exceed the limits of the Knudsen region. A more sensitive potentiometer, and a more stable and more sensitive balance are necessary for the utilization of this technique.

LITERATURE CITED

1. M. Knudsen, Ann. Physik, 28, 999 (1909); Chem. Abstr., 3, 1839 (1909).

2. J. L. Margrave in "Physicochemical Measurements at High Temperatures," J. O'M. Bockris, J. L. White, and J. D. Mackenzie, Ed., Butterworths Scientific Publications, London, 1959, Chapter Ten.

3. P. Clausing, Ann. Physik, 12, 961 (1932); Chem. Abstr., 26, 3311 (1932).

4. R. P. Iczkowski, J. L. Margrave, and S. M. Robinson, J. Phys. Chem., 67, 229 (1963).

5. R. D. Freeman, "Molecular Flow and the Effusion Process in the Measurement of Vapor Pressures," Technical Documentary Report No. ASD-TDR-63-754, Office of Technical Services, U. S. Department of Commerce, Washington, D. C., 1963.

6. K. Motzfeldt, J. Phys. Chem., 59, 139 (1955).

7. G. Rosenblatt, J. Electrochem. Soc., 110, 563 (1963).

8. W. Fischer, R. Gewehr, and H. Wingchen, Z. Anorg. Allg. Chem., 242, 161 (1939).

9. L. H. Spinar, Ph.D. Thesis, University of Wisconsin, Madison, Wisconsin, 1957.

10. C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," 39th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1958, pp 2410-2412.

11. ibid, p 2152.

12. K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy," Bureau of Mines Bulletin, 383, U. S. Government Printing Office, Washington, D. C., 1935, p 108.

13. M. D. Taylor and C. P. Carter, J. Inorg. Nucl. Chem., 24, 387 (1962).

14. W. W. Wendlandt, J. Inorg. Nucl. Chem., 5, 118 (1957).

15. F. Petru, J. Hradilova, and B. Hajek, Collect. Czech. Chem. Commun., 33, 2720 (1968).

16. American Society for Testing Materials, "X-ray Powder Data File," 1966, Card No. 7-89.

17. H. E. Swanson, R. K. Fuyat, and G. M. Urgrinic, "Standard X-ray Diffraction Powder Patterns," U. S. National Bureau of Standards Circular 539, Vol. III, U. S. Government Printing Office, Washington, D. C., 1954, p 27.

18. F. Petru, J. Koslerova, and B. Hajek, Z. Chem., 6, 229 (1966).

19. E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd ed, Interscience Publishers, Inc., New York, N. Y., 1959, p 797.

20. J. L. Moriarity, J. Chem. Eng. Data, 8, 422 (1963).